

Diketopyrrolopyrrole-based Conjugated Polymers as Additives to Optimize Morphology for Polymer Solar Cells*

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Abstract Novel random copolymers for optimizing the morphology of the active layer for high performance organic photovoltaic devices have been demonstrated. Three ternary random copolymers PTBDTPPSPiCN(3/7), PTBDTPPSPiCN(5/5), PTBDTPPSPiCN(7/3) were prepared by polymerization of electron-donating thienyl-substituted benzodithiophene (TBDT) with 2,5-bis[8-(1,1,3,3,5,5,5-heptamethyltrisiloxane-3-yl)octyl]-pyrrolo[3,4-c]pyrrole-1,4-dione (DPPSi) and 2,5-dio[5-(5-cyano-5,5-dimethyl-pentyl)]-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (DPPCN) of different ratios. The DPPCN block can well-tune the light absorption and molecular packing, while the DPPSi block is in favor of enhancing the charge mobility. And the formation of organic Si—O—Si networks is beneficial to stabilize the morphology of the active layer. These new copolymers have narrow bandgaps and broaden visible light absorption from 500 nm to 1000 nm. Careful balance of the contents of the trimethoxysilyl group and the cyano group can well-tune the surface energy and morphology of the copolymers. Incorporation of these novel copolymers as additives into the blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₀-butyric acid methyl ester (PC₆₁BM) is found to effectively broaden the light absorption, improve the compatibility and morphology of the active layer. As a result, some devices with certain ratios of these copolymers as additives achieve the enhanced efficiency compared with the device based on pristine P3HT:PC₆₁BM.

Keywords: Ternary random copolymers; Additive; Morphology; Polymer solar cells.

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INTRODUCTION

In the past decades, polymer solar cells (PSCs) have attracted considerable attention as promising energy resources because of they allow the production of low cost, light weight, large area, flexible devices through ink jet printing and roll to roll solution processing^[1–3]. To date, the bulk heterojunction (BHJ) architecture cell has attracted the interests of many people because of its high power conversion efficiencies (PCEs). Among the various material systems of BHJ architecture cells, the blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₀-butyric acid methyl ester (PC₆₁BM) is one of the most widely studied. Over the past few years, a great amount of research effort has been focused on the classical blend system of P3HT donor and PC₆₁BM acceptor, and significant enhancement for the efficiency has been achieved^[4–8]. The power conversion efficiency of P3HT/PC₆₁BM solar cells has been well optimized in a variety of ways^[9]. But the bad compatibility between

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P3HT and PC₆₁BM made the film morphology perishing, which leads to the formation of large phase separation and hamper exciton dissociation and charge transport. In addition, the mismatching of solar flux and P3HT/PC₆₁BM absorption spectrum limits the enhancement of PCEs. Meanwhile, the PSCs still suffer from the cell degradation mainly due to instability of the materials and morphology of the active layer. Tremendous efforts focus on optimization of self-assembly or phase separation in the P3HT:PC₆₁BM blend to obtain a well-defined and stable morphology. Among various approaches, incorporation of a polymeric additive has been regarded as a promising method to improve the device performance^[10]. Recently, it has been proven that polymers with trimethoxysilyl groups could effectively tune the morphology when added as additives to the active layer. Han *et al.* synthesized an asymmetric rod-coil block copolymer that consists of P3HT as the majority block and poly[(3-trimethoxysilyl)propyl methacrylate (PTMSM) as the minority block. Adding the block copolymer (P3HT-*b*-PTMSM) into the P3HT/PC₆₁BM mixture followed by brief thermal treatment, the trimethoxysilyl groups of the PTMSM block can be transformed to SiO_x-like residues. Upon evaporation of the solvent, the PTMSM blocks sitting at the interfacial regions between the P3HT and PC₆₁BM domains, acting as a blocking layer to depress the recombination of charge carriers, affording about a 50% enhancement of the power conversion efficiency over the devices without the copolymer^[11]. Besides, the effectiveness of siloxanes side chains on morphology, molecular packing and charge transport of conjugated polymers has also been improved. Lee *et al.* also prepared a new donor-acceptor (D-A) copolymer PTDPSe-SiC5 based on diketopyrrolopyrrole (DPP) blocks containing the hybrid siloxane substituents on nitrogen atoms of the DPP motif. The resulting polymer showed extremely high hole and electron mobilities of 8.84 and 4.34 cm²·V⁻¹·s⁻¹^[12, 13]. Similarly, Bao *et al.* have successfully proven the effectiveness of siloxane as the side chains in an isoindigo containing polymer for enhancing charge transport^[14]. In addition, through side-chain functional modification, the morphology of copolymers has been successfully tuned, thus improving their device performance^[15, 16].

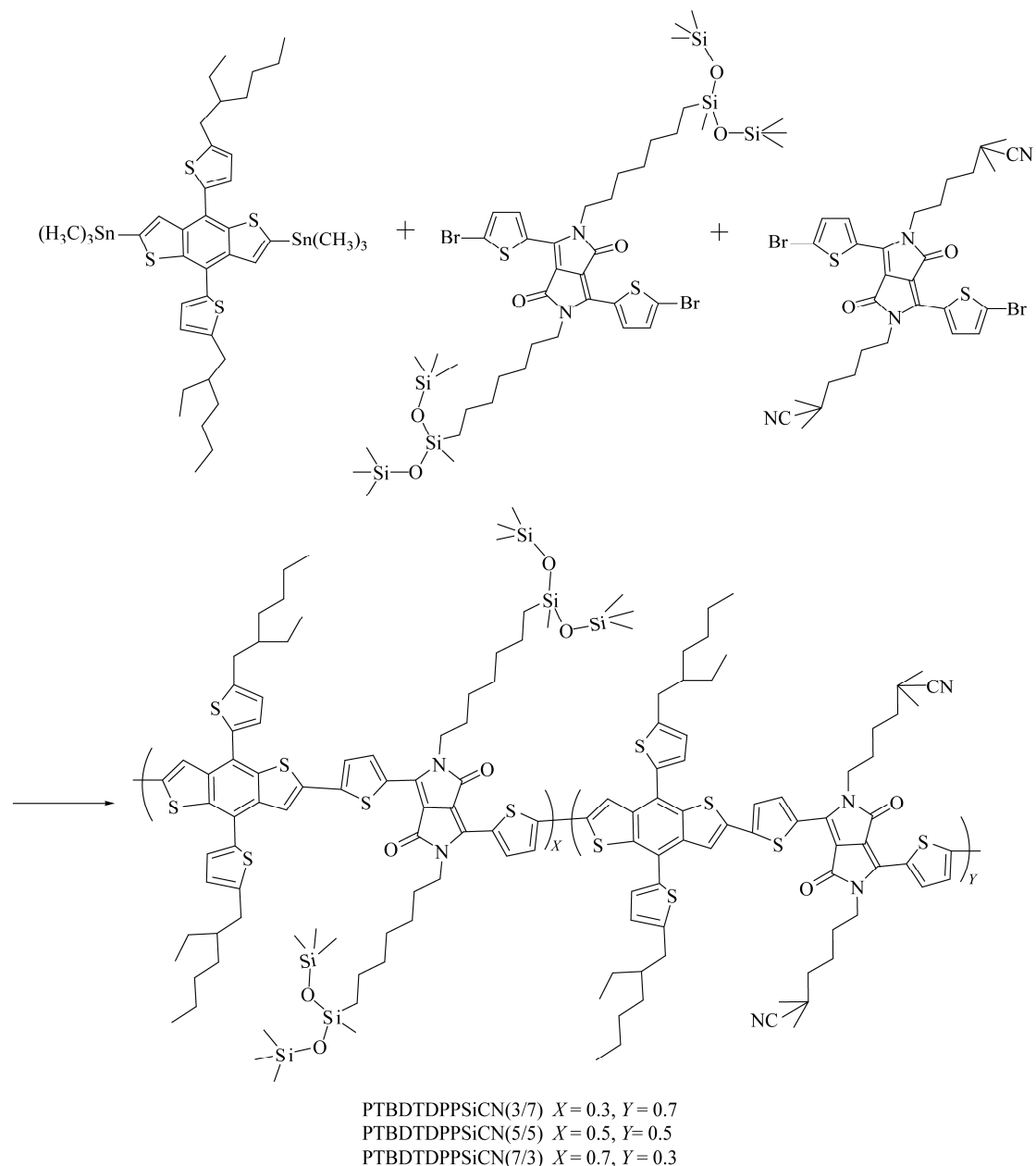
These encouraging results inspire us to develop new siloxane side chains containing polymers with narrow bandgap for solar cells aiming at improving the optical absorption and tuning the morphology of P3HT/PC₆₁BM system when they are added as additives to the active layer. Meanwhile, the trimethoxysilyl groups of polymers efficiently undergo a condensation reaction and are cross-linked to yield organic Si—O—Si networks under the condition of thermal annealing normally, which is beneficial to stabilize the morphology of the active layer. However, the introduction of siloxane units will reduce the surface energy of resulted polymers through stratifying the surface during the film formation and cross-linking^[17]. Thus, bring siloxane side chains to polymer backbone may influence the blending of polymer and fullerenes acceptor. By report, the high polarity of the cyano-group will help to increase the surface energy^[15]. Therefore, the surface energy of polymers can be adjusted to a proper value by varying the ratio of siloxanes and cyano groups to match the surface energy of fullerenes acceptor.

Herein, we prepared two functional DPP monomers 2,5-bis[8-(1,1,3,3,5,5,5-heptamethyltrisiloxane-3-yl)octyl]-pyrrolo[3,4-c]pyrrole-1,4-dione (DPPSi) and 2,5-dio[5-(5-cyano-5,5-dimethyl-pentyl)]-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (DPPCN), which contain siloxanes and cyano groups respectively. And three ternary random copolymers with narrow bandgaps, PTBDTDPPSiCN(3/7), PTBDTDPPSiCN(5/5), PTBDTDPPSiCN(7/3), have been prepared by polymerization of DPPCN and DPPSi with electron-donating thienyl-substituted benzodithiophene (TBDT) with the different ratios of DPPCN and DPPSi (Scheme 1, Scheme S1). In view of the function of siloxane and cyano groups and the strong stacking of DPP-TBDT backbones, the incorporation of these polymer additives into the active layer is expected to enhance the optical absorption and optimize the phase-separated microscopic P3HT and PC₆₁BM domains and the stability. Additionally, with a well matched energy level of P3HT and PC₆₁BM, the additive can be regarded as a bridge for charge transfer between P3HT and PC₆₁BM, contributing to the transmission of charge carriers.

EXPERIMENTAL

Materials

3,6-Dithiophen-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP), 1-dromo-6-cyano-5,5-dimethyl-hexane, 1,1,3,3,5,5,5-heptamethyltrisiloxane, tetrabutyl ammonium tribromide, 8-bromo-oct-1-ene, $\text{Pd}_2(\text{dba})_3$, $\text{P}(\text{o-tol})_3$, Karstedt's catalyst (platinum-divinyltetramethyl-siloxane complex in xylene, 3 wt%), 2,6-bis(trimethyl-selenium)-4,8,-di(ethylhexyl-2-thiophene)benzene[1,2-b:4,5-b']-thio-phen, PC_{61}BM (99.9%) and other materials were purchased from Alfa Aesar, or Aldrich and used without further purification. Indium-tin oxide (ITO) glass was purchased from Delta Technologies Limited.



Scheme 1 Synthesis of the novel ternary copolymers

Preparation of Monomers

2,5-Dio[5-(5-cyano-5,5-dimethyl-pentyl)]-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (**1**)

A mixture of 3,6-dithiophen-2-yl-2,5-dihydro-pyrrolo[3,4-c] pyrrole-1,4-dione (1.00 g, 3.3 mmol) and anhydrous K_2CO_3 (1.50 g, 10.9 mmol) was dissolved in 40 mL anhydrous DMF and heated to 120 °C under N_2 for 1 h. To the resulting solution, 1-bromo-6-cyano-5,5-dimethyl-hexane (1.73 g, 8.5 mmol) was added dropwise and then the mixture was stirred under N_2 at 130 °C for 24 h. After cooling to room temperature, the reaction solution was poured into cold water (300 mL) and extracted with chloroform three times. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The residue was further purified on the silica gel column by eluting with $CHCl_3$:hexane = 2:1 to afford **1** as a dark red solid (1.44 g, 80%). ^1H -NMR ($CDCl_3$, 600 Hz, δ): 8.91 (d, 2H), 7.67 (t, 2H), 7.30 (m, 2H), 4.11 (m, 4H), 1.78 (t, 4H), 1.59 (m, 4H), 1.33 (s, 12H), 1.31 (m, 4H).

3,6-Bis-(5-bromo-thiophen-2-yl)-2,5-(5-cyano-5,5-dimethyl-pentyl)-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (**2**)

A solution of **1** (0.546 g, 1 mmol) in $CHCl_3$ (50 mL) was stirred at room temperature (RT) for 2 h under nitrogen before *n*-bromosuccinimide (0.41 g, 2.3 mmol) was added in portions. The mixture was kept in the dark for 24 h and then quenched with methanol (200 mL). The crude solid was collected by vacuum filtration and washed with water and methanol. Following that, the residue was further purified on the silica gel column using $CHCl_3$ as the eluent to afford compound **2** as a dark red solid (0.436 g, 62%). ^1H -NMR ($CDCl_3$, 600 Hz, δ): 8.62 (d, 2H), 7.27 (t, 2H), 4.0 (m, 4H), 1.76 (t, 4H), 1.58 (m, 4H), 1.19 (s, 12H), 0.86 (m, 4H).

2,5-Di-oct-7-enyl-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (**3**)

To a suspension of 3,6-dithiophen-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP) (1.05 g, 3.5 mmol) and potassium carbonate (1.93 g, 14.0 mmol) in anhydrous dimethylformaldehyde (DMF) (50 mL), 8-bromo-oct-1-ene (1.56 g, 8.4 mmol) was injected through a septum under nitrogen. The mixture was stirred for 24 h at 100 °C and then poured into water (300 mL) and stirred for 0.5 h. The organic phase was extracted by CH_3Cl_3 , washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the deep-red solids were purified by silica chromatography, eluting with CH_2Cl_2 :hexane = 1:1 (monomer **3**, yield 70%). ^1H -NMR ($CDCl_3$, 600 Hz, δ): 8.94 (d, 2H), 7.64 (t, 2H), 7.29 (m, 2H), 5.78 (t, 2H), 4.94 (s, 4H), 4.06 (t, 4H), 2.05 (m, 4H), 1.76 (m, 4H), 1.56 (m, 4H), 1.42–1.16 (m, 8H).

2,5-Bis[8-(1,1,3,3,5,5,5-heptamethyltrisiloxane-3-yl)octyl]-pyrrolo[3,4-c]pyrrole-1,4-dione (**4**)

Compound **3** (0.95 g, 1 mmol) was dissolved in anhydrous toluene (15 mL) under an argon atmosphere. 1,1,3,3,5,5,5-heptamethyltrisiloxane (0.96 g, 4.6 mmol) was injected through a septum, followed by the addition of a drop (20 μ L) of Karstedt's catalyst (platinum-divinyltetramethyl-siloxane complex in xylene, 3 wt%). The resulting mixture was stirred at 50 °C under argon till complete consumption of compound **3**. The solution was directly subjected to silica gel chromatography using CH_2Cl_2 :hexane (2:3) as an eluent, yielding dark red oil (monomer **4**) which was solidified over the time (yield, 50%). ^1H -NMR ($CDCl_3$, 600 Hz, δ): 8.93 (d, 2H), 7.62 (t, 2H), 7.29 (m, 2H), 4.05 (t, 4H), 1.75 (m, 4H), 1.41 (m, 8H), 1.29 (m, 12H), 0.92 (d, 36H), 0.43 (s, 6H).

3,6-Bis-(5-bromo-thiophen-2-yl)-2,5-bis[8-(1,1,3,3,5,5,5-heptamethyltrisiloxane-3-yl)octyl]-3,6-dithiophen-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (**5**)

A solution of **4** (0.95 g, 1 mmol) in $CHCl_3$ (50 mL) was stirred at room temperature (RT) for 2 h under nitrogen before tetrabutyl ammonium tribromide (1.1 g, 2.3 mmol) was added in portions. The mixture was kept in dark for 24 h and then quenched with methanol (200 mL). The solid mixture was collected by vacuum filtration and washed with water and methanol. Following that, the crude solid was purified on the silica gel column using $CHCl_3$ as the eluent to afford compound **5** as a dark oil solid (yield, 30%). ^1H -NMR ($CDCl_3$, 600 Hz, δ): 8.67 (d, 2H), 7.25 (t, 2H), 3.96 (t, 4H), 1.68 (m, 4H), 1.49 (m, 8H), 1.29 (m, 12H), 0.85 (d, 36H), 0.41 (s, 6H).

Preparation of Polymers

PTBDTDPPSiCN(3/7)

2,6-Bis(trimethylselenium)-4,8-di(ethylhexyl-2-thiophene) benzene [1,2-b:4,5-b'] thiophene (TBDT) (100 mg, 0.11 mmol), compounds **5** (85.5 mg, 0.077 mmol) and **2** (23 mg, 0.033 mmol) were dissolved in dry anhydrous toluene (8 mL) and the solution was carefully degassed before the addition of Pd₂(dba)₃ (4 mg) and P(o-tol)₃ (8 mg). The resulting solution was heated to 110 °C and stirred under N₂ for 48 h. The reaction mixture was allowed to cool down to RT and subsequently added dropwise into methanol (200 mL). The precipitation was obtained by vacuum filtration and then washed by Soxhlet extraction with acetone and hexane. The solid was then redissolved in chloroform and then precipitated again from hexane. Vacuum filtration and drying afforded the polymer PTBDTDPPSiCN(3/7) as a dark black solid (yield, 80%). ¹H-NMR (CDCl₃, 600Hz, δ): 7.52 (d, 2H), 7.3 (d, 2H), 7.25 (d, 4H), 6.99 (d, 2H), 2.95 (t, 4H), 2.04 (t, 2H), 1.7 (m, 2H), 1.5 (m, 38H), 1.25 (m, 16H), 1.1–0.8 (m, 16H), 0.7 (s, 27H), 0.14 (s, 2H), 0.06 (s, 16H). *M_w* = 2.37 kg/mol, *M_n* = 1.12 kg/mol, PDI = 2.11.

PTBDTDPPSiCN(5/5)

PTBDTDPPSiCN(5/5) was prepared from (TBDT) (100 mg, 0.11 mmol), monomer **5** (55.5 mg, 0.05 mmol), monomer **2** (35 mg, 0.05 mmol) using the same method as for PIDTDPPSiCN(3/7) with a yield of 82%. ¹H-NMR (CDCl₃, 600 Hz, δ): 7.52 (d, 2H), 7.3 (d, 2H), 7.25 (d, 4H), 6.99 (d, 2H), 2.95 (t, 4H), 2.04 (t, 2H), 1.7 (m, 2H), 1.5 (m, 32H), 1.25 (m, 16H), 1.1–0.8 (m, 18H), 0.7 (s, 27H), 0.14 (s, 3H), 0.06 (s, 27H). *M_w* = 2.59 kg/mol, *M_n* = 1.31 kg/mol, PDI = 1.98.

PTBDTDPPSiCN(7/3)

PTBDTDPPSiCN(7/3) was prepared from (TBDT) (100 mg, 0.11 mmol), monomer **5** (33.3 mg, 0.03 mmol), monomer **2** (49.3 mg, 0.07 mmol) using the same method as for PIDTDPPSiCN(3/7) with a yield of 80%. ¹H-NMR (CDCl₃, 600Hz, δ): 7.52 (d, 2H), 7.3 (d, 2H), 7.25 (d, 4H), 6.99 (d, 2H), 2.95 (t, 4H), 2.04 (t, 2H), 1.7 (m, 2H), 1.5 (m, 27H), 1.25 (m, 16H), 1.1–0.8 (m, 20H), 0.7 (s, 27H), 0.14 (s, 4H), 0.06 (s, 38H). *M_w* = 2.43 kg/mol, *M_n* = 1.39 kg/mol, PDI = 1.75.

Characterization

The ¹H-NMR measurements were performed on a Bruker ARX 400/600 MHz NMR workstation. Molecular weights of the polymers were determined by a Waters 2414 gel permeation chromatograph (GPC) with a refractive index detector in CHCl₃ using a calibration curve of polystyrene standards. Cyclic voltammetry (CV) measurements were carried out on a CHI 660C electrochemical workstation equipped with three-electrode cell using platinum electrodes and a Ag/Ag⁺ (0.1 mol/L of AgNO₃ in acetonitrile) reference electrode in an anhydrous and argon-saturated solution of 0.1 mol/L of tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) in acetonitrile at a scan rate of 50 mV/s. Under these conditions, the oxidation potential (*E*_{OX 1/2}) of ferrocene was −0.02 eV versus Ag/Ag⁺. The HOMO energy level of polymers was determined from the oxidation onset of the second scan from CV data. It is assumed that the redox potential of Fc/Fc⁺ has an absolute energy level of −4.50 eV to vacuum. The energy of HOMO and LUMO levels were calculated according to the Eqs. (1) and (2), the electrochemically determined band gaps were deduced from the difference between onset potentials from oxidation and reduction of copolymers as given by Eq. (3).

$$E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{ox}} + 4.50) \text{ (eV)} \quad (1)$$

$$E_{\text{LUMO}} = -(E_{\text{onset}}^{\text{red}} + 4.50) \text{ (eV)} \quad (2)$$

$$E_{\text{g}}^{\text{ec}} = (E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}) \text{ (eV)} \quad (3)$$

Annealing of films was conducted by heating in the setting temperature for 10 min, followed by cooling to room temperature at a cooling speed of 1 K/min. The polymer solid films were cast from chlorobenzene (CB) solution and the ultraviolet-visible (UV-Vis) absorption spectra of polymer thin films were measured using a PerkinElmer Lambda 750 spectrophotometer. Thermogravimetric analysis (TGA) measurements were carried out with a PerkinElmer TGA 7 for thermogravimetry at a heating rate of 10 K/min under nitrogen. The X-ray

diffraction (XRD) study of the copolymers was performed on a Bruker D8 Focus X-ray diffractometer operating at 30 kV and 20 mA with a copper target ($\lambda = 0.154$ nm) and at a scanning rate of 1 ($^{\circ}$)/min. Atomic force microscopic (AFM) images were measured on a Nanoscope III A (Digital Instruments) scanning probe microscope using the tapping mode. Current-voltage (J - V) characteristics were recorded using a Keithley 2400 Source Meter in the dark and under 100 mW/cm² simulated AM 1.5 G irradiation (Abet Solar Simulator Sun 2000).

PSCs with a forward device structure were fabricated. Patterned ITO-glass substrates were used as the cathode in the PSCs. The ITO coated glass substrates were cleaned by ultrasonic washing in acetone, detergent, deionized water, and isopropyl alcohol and then dried by N₂ flow and subjected to the treatment of UV ozone over 20 min. ZnO precursor thin layer was spin-coated on the ITO surface at 4000 r/min for 60 s, slowly dried for 2 h under N₂ conditions. And then, similarly, the BHJ composite layer, P3HT:PC₆₁BM:polymer (with different ratios), was cast on the ZnO layer at 800 r/min for 30 s and 1400 r/min for 2 s from CB solution with 10 mg/mL and slowly dried for 2 h and followed with thermal annealing at 150 $^{\circ}$ C for 10 min under N₂ conditions. The thickness of the BHJ composite layer is about 80 nm. Subsequently, MoO₃ (0.7 nm) and Ag (900 nm) electrodes were deposited *via* thermal evaporation in vacuum in thickness of approximately layers. The effective area of the devices was measured to be 0.04 cm². The thicknesses of all the films were measured by a Dektak profiler. Annealed devices was conducted by heating at 150 $^{\circ}$ C for 10 min, followed by cooling to room temperature at a cooling speed of 1 K/min. Current-voltage (J - V) characteristics were recorded using a Keithley 2400 Source Meter in the dark and under 100 mW/cm² simulated AM 1.5 G irradiation (Abet Solar Simulator Sun 2000). All the measurements were performed under ambient atmosphere at room temperature.

RESULTS AND DISCUSSION

Thermal Stability

The trimethoxysilyl groups of polymers efficiently undergo a condensation reaction to yield organic Si—O—Si networks under the condition of thermal annealing normally performed in the PSC fabrication. As shown in Fig. 1, the thermogravimetric analysis (TGA) result reveals that the onset points of the weight loss are at the temperature $\sim$ 130 $^{\circ}$ C, indicating the condensation of siloxane side chains. That is also confirmed by the temperature increased with the enhancement of the content of DPPSi. The formation of organic Si—O—Si networks is beneficial to stabilize the morphology of the active layer.

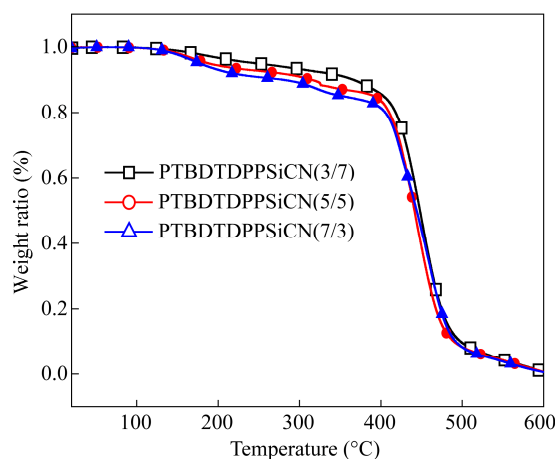


Fig. 1 TGA curves of polymers with a heating rate of 10 K/min

Optical Properties

The photophysical characteristics of the polymers and ternary blends of P3HT:PC₆₁BM:copolymers were investigated by ultraviolet-visible (UV-Vis) absorption spectroscopy in dilute chloroform solutions and as spin-coated films on quartz substrates. As shown in Fig. 2, all the polymers show similar features with a broad absorption band extended from 500 nm to 1000 nm, which is attributed to the intramolecular charge transfer arising from strong donor-acceptor interactions. In low energy band, PTBDTDPPSiCN(7/3) showed much stronger absorbance in the region of 400–550 nm than PTBDTDPPSiCN(3/7) and PTBDTDPPSiCN(5/5), which could be due to the stronger localized π - π^* transitions in PTBDTDPPSiCN(7/3), as shown in Fig. 2(a). And a pronounced red shift of the absorption peak is observed when going from solution to the solid state, suggesting the increase of intermolecular interaction of polymer chains in the solid state. The $\lambda_{\max}$ bands of the polymers are located at 750–800 nm, which match well with the solar flux. The optical properties of the polymers are shown in Table 1. The corresponding optical band gaps of the polymer PTBDTDPPSiCN(3/7), PTBDTDPPSiCN(5/5) and PTBDTDPPSiCN(7/3) are estimated to be 1.42, 1.44 and 1.47 eV respectively, according to the absorption edge of these films. Notably, caused by the electrophilic CN group, PTBDTDPPSiCN(3/7) with high content of CN exhibits a relatively red shifted $\lambda_{\max}$ band and narrower band gap compared to PTBDTDPPSiCN(5/5) and PTBDTDPPSiCN(7/3), indicating the electrophilic CN is favorable to molecular packing, subsequently reducing the bandgap and broadening the absorption band of the polymers.

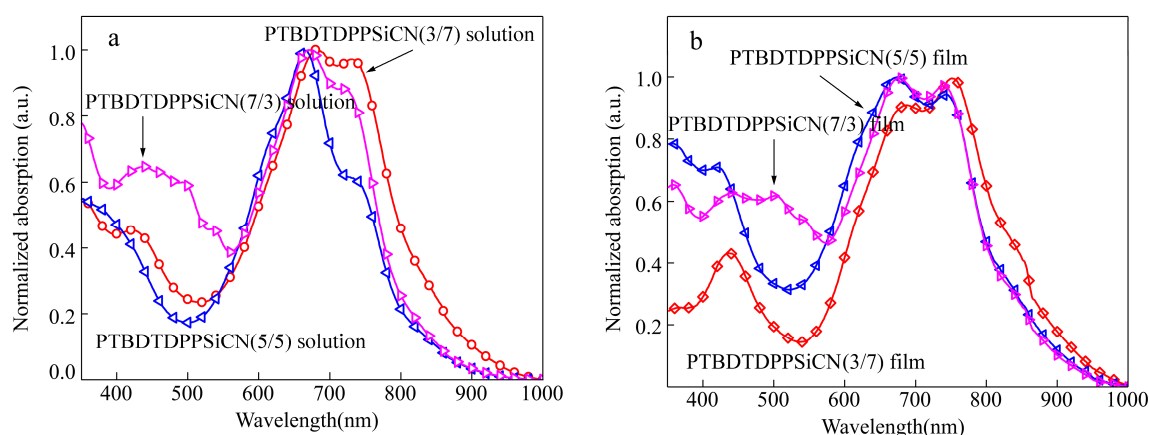


Fig. 2 UV-Vis absorption spectra of copolymers in CHCl₃ solution (a) and in the solid state (b)

Table 1. Optical properties of the copolymers

Polymers	$\lambda_{\max}$ (nm)		λ_{onset} (nm)	E_g^{opt} (eV)
	Solution	Film	Film	
PTBDTDPPSiCN(3/7)	733	753	872	1.42
PTBDTDPPSiCN(5/5)	733	742	861	1.44
PTBDTDPPSiCN(7/3)	718	738	842	1.47

Electrochemical Properties

The electrochemical properties of the copolymers were investigated with cyclic voltammetry (CV). Figure 3(a) shows the cyclic voltammograms which were measured using a Pt counter electrode and an Ag/AgCl reference electrode in a 0.1 mol/L electrolyte containing tetrabutylammonium hexafluoro-phosphate in acetonitrile with a scan rate of 50 mV/s. The data are presented in Table 2, and the results are consistent with the aforementioned optical properties. PTBDTDPPSiCN(3/7) shows the lowest lying LUMO level of -3.73 eV and the smallest band gap of 1.60 eV due to the high content of CN groups. With the increase of siloxanes content, the HOMO level decreases from -5.33 eV for PTBDTDPPSiCN(3/7) to -5.35 eV for PTBDTDPPSiCN(5/5), and then to -5.36 eV for PTBDTDPPSiCN(7/3). In addition, the observed differences in LUMO levels result from the changes in film microstructure caused by different side chains. Notably, the effect of changing the side chain of

the conjugated backbone is more pronounced on the LUMO than on the HOMO, as seen in Table 2. This may be correlated partly with the different degrees of intermolecular interaction between the polar siloxane-terminated or CN-terminated groups with the main backbones in the solid state. Although there is variation in energy levels caused by the different ratios of siloxanes and CN groups, but the energy level of these polymers is well matching the energy level of P3HT and PC₆₁BM, therefore they can regard as a bridge for charge transfer between P3HT and PC₆₁BM. At the same time, the narrow bandgaps of the copolymers can compensate the light absorption at long wavelengths from 700 nm to 1000 nm, where P3HT can not absorb. The corresponding energy level diagram of the components of the devices is presented in Fig. 3(b).

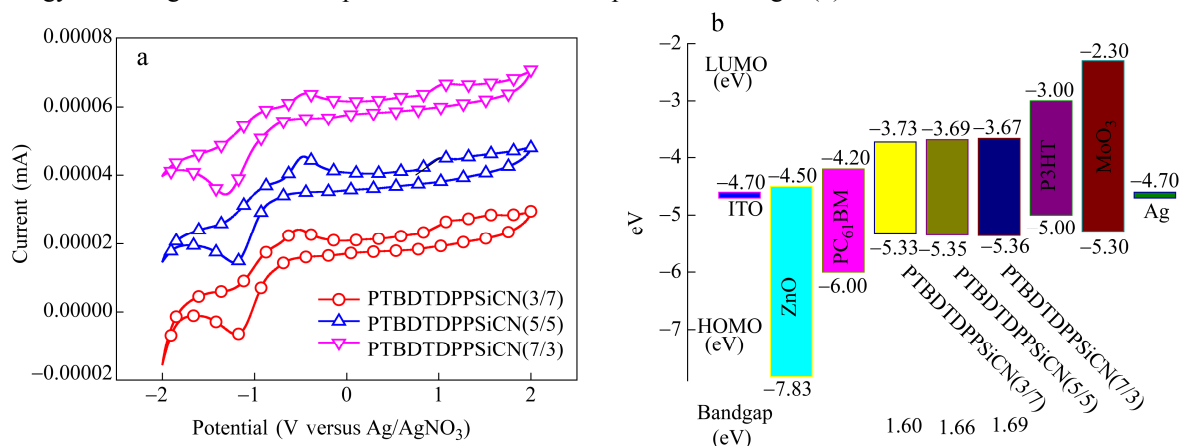


Fig. 3 (a) Cyclic voltammetry (CV) of polymer films coated on platinum electrode; (b) The corresponding energy level diagram of the components of the devices

Table 2. Electrochemical properties of the copolymers

Polymers	$E_{\text{onset}}^{\text{ox}}$ (eV)	$E_{\text{onset}}^{\text{red}}$ (eV)	HOMO (eV)	LUMO (eV)	E_g (eV)
PTBDTDPPSiCN(3/7)	0.83	-0.77	-5.33	-3.73	1.60
PTBDTDPPSiCN(5/5)	0.85	-0.81	-5.35	-3.69	1.66
PTBDTDPPSiCN(7/3)	0.86	-0.83	-5.36	-3.67	1.69

Surface Properties

Surface properties of the individual components in the BHJ layer are very critical in determining their compatibility in the blend. BHJ film morphology mostly relies on the miscibility between the donor and acceptor molecules^[18, 19], which is strongly associated with the surface energy of blending components^[20–22]. However, the surface energy of P3HT is measured to be 23.9 mN/m^[23] and that of PC₆₁BM is to be 34.2 mN/m^[22], thus the quite different surface energies between the P3HT and PC₆₁BM lead to a poor miscibility of the two components. Since the novel copolymer is designed to mediate the morphology of the P3HT:PC₆₁BM, we hope that the surface energy in the active layer can be eliminated by incorporation of the copolymer additives. Therefore, contact angle tests were performed on polymer films to investigate the surface energy of the novel copolymers. The surface energy of copolymer films can be calculated by the following equation:

$$\begin{aligned}\gamma_1 (1 + \cos\theta_{\text{water}}) &= 2(\gamma_{\text{D}}\gamma_{\text{P}})^{1/2} + 2(\gamma_{\text{P}}\gamma_{\text{P}})^{1/2} \\ \gamma_2 (1 + \cos\theta_2) &= 2(\gamma_{\text{D}}\gamma_{\text{D}})^{1/2} + 2(\gamma_{\text{P}}\gamma_{\text{P}})^{1/2} \\ \gamma_{\text{S}} &= \gamma_{\text{D}} + \gamma_{\text{P}}\end{aligned}$$

γ_{S} represents the surface energy of polymer film, γ_{D} represents the dispersion force, and γ_{P} represents the polarity force. γ_1 and γ_2 represent the surface tension of the two testing liquids, including the dispersion item and polar item, there are the following relationships between them: $\gamma_1 = \gamma_{\text{D}} + \gamma_{\text{P}}$; $\gamma_2 = \gamma_{\text{D}} + \gamma_{\text{P}}$. On the conditions that the values of γ_{D} , γ_{P} , γ_{D} and γ_{P} were given, the γ_{D} and γ_{P} can be obtained by determining θ_{water} and θ_2 . Therefore, the surface energy of γ_{S} can be obtained. The test used water (1) and CH₂I₂ (2) as the liquids.

Water:

$$\gamma_{1D} = 26.4 \text{ mN/m}$$

$$\gamma_{1P} = 46.4 \text{ mN/m}$$

$$\gamma_1 = 72.8 \text{ mN/m}$$

CH₂I₂:

$$\gamma_2 = \gamma_{2D} = 50.8 \text{ mN/m}$$

$$\gamma_{2P} = 0$$

Corresponding data are summarized in Table 3. In general, the surface roughness of the film structure increases as the raise of siloxane ratio, which means increasing siloxane ratio will decrease surface energy^[17]. However, the high polarity of the cyano group will increase the surface energy^[15]. As the ratio of DPPSi content increases, the contact angle values increase and the overall surface energy decreases. As a result, the surface energy of PTBDTDPPSiCN(3/7), PTBDTDPPSiCN(5/5) and PTBDTDPPSiCN(7/3) is 28.5, 26.1 and 23.7 mN/m respectively. Delightfully, the surface energy values of PTBDTDPPSiCN(3/7) and PTBDTDPPSiCN(5/5) are exactly between those of the P3HT and PC₆₁BM. It is believed that the closer surface energy of the individual components in a BHJ is helpful for better miscibility to develop a more homogeneously mixed blend (to be discussed later).

Table 3. Surface energy parameters of copolymers

Polymer	θ_{water}	θ_2	γ_D (mN/m)	γ_P (mN/m)	γ (mN/m)
PTBDTDPPSiCN(3/7)	88.5	32.5	24.5	4.0	28.5
PTBDTDPPSiCN(5/5)	96	33.5	24.3	1.8	26.1
PTBDTDPPSiCN(7/3)	100	40.5	22.4	1.3	23.7

Thin-Film Microstructure Analyses

In general, donor-acceptor (D-A) type polymers have a tendency to form inter-chain aggregates by virtue of strong π - π stacking, which leads to efficient charge transport in devices^[24, 25]. X-ray diffraction (XRD) analyses were performed to investigate the crystallinity and molecular organization in thin films of copolymers. The XRD spectra of the polymers are shown in Fig. 4(a), where four highly resolved diffraction peaks in the region of 2°–30° can be detected. Distinct primary diffraction features are observed at 2 θ of ~4.4° and the intensity increases from PTBDTDPPSiCN(3/7) to PTBDTDPPSiCN(7/3), which corresponds to the layer distance. The shortest distance of layer stacking for PTBDTDPPSiCN(7/3) can be ascribed to the increased content of DPPSi units on polymer, because the branched siloxane side chain will enhance the denser molecular packing layer by

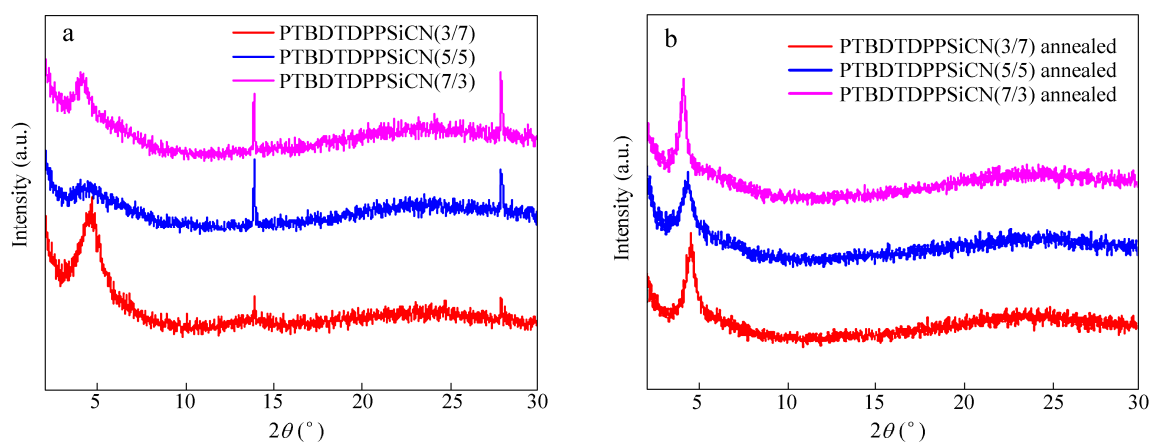


Fig. 4 X-ray diffraction patterns of copolymer films as cast (a) and after thermal annealing at 150 °C for 10 min (b)

layer interaction^[11]. Meanwhile, there is a similar intense and sharp primary diffraction peak at $2\theta = \sim 27.85^\circ$ for these polymers, corresponding to $d_{(010)}$ spacing value of ~ 0.32 nm and attributed to π - π stacking reflection. The $d_{(010)}$ -spacing of polymers is smaller than that of the classical material P3HT (0.38 nm)^[26]. The highly organized polymer chains in the thin films are expected to be particularly favorable for charge transport in a PSC device. However, it is strange that the diffraction peak of π - π stacking disappears after annealing at 150 °C (Fig. 4b). It is therefore anticipated that the polymer films would be able to adopt 3D conduction channels to enhance charge transport over that of polymer films with only perpendicular π - π planes^[27].

Morphology

To evaluate the morphology change of the P3HT:PC₆₁BM caused by addition of the novel copolymers, AFM has been employed. P3HT:PC₆₁BM:copolymer (3 wt%) blend films were prepared using the same procedure to the device fabrication. Figure 5 displays the topography images in height, and Fig. S7 shows the topography in 3D images of the blend films after annealing. As shown in Fig. 5, the image of the P3HT:PC₆₁BM blend film shows coarse grained phase separation with a surface roughness of 6.57 nm. When a small amount of copolymers is added into the P3HT:PC₆₁BM blend, all the modified films show the sharply reduced surface roughness of 1.48–3.39 nm with better micro-phase separation morphology, especially for PTBDTDPPSiCN(3/7) and PTBDTDPPSiCN(5/5) contained films. The improved morphology can promote the efficient exciton separation and charge transportation. This finding also suggests that the relative content of DPPSi and DPPCN plays an important role on controlling the morphology arrangement, and the DPPCN is more favorable for molecular packing, in agreement with the UV observation. In addition, seen from Fig. 6, a pronounced red shifted absorption (~ 30 nm) in the absorption band with a stronger shoulder peak at ~ 600 nm is observed, when the mass ratio of 3 wt% of PTBDTDPPSiCN(3/7) is introduced into P3HT:PC₆₁BM blend. This observation indicates that the polymeric additive can promote molecular packing and thin-film morphology, which may in turn have a significant effect on PCE of PSC.

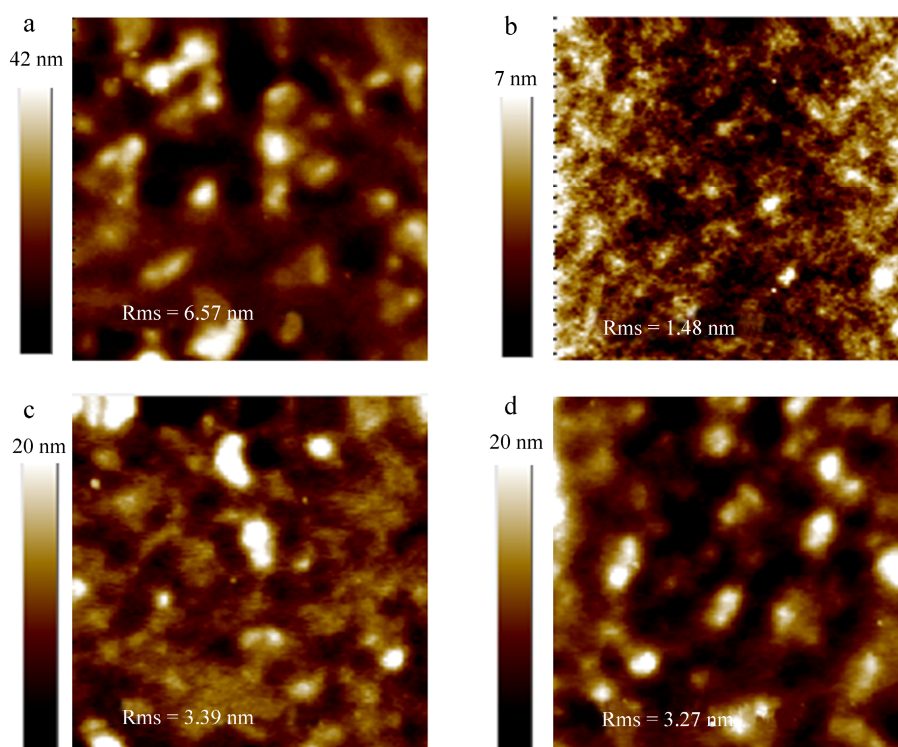


Fig. 5 Tapping mode AFM height images of the films based on P3HT:PC₆₁BM and P3HT:PC₆₁BM:3 wt% PTBDTDPPSiCN after annealing at 150 °C for 10 min (3 $\mu\text{m} \times 3 \mu\text{m}$): (a) P3HT:PC₆₁BM, (b) P3HT:PC₆₁BM:3 wt% PTBDTDPPSiCN(3/7), (c) P3HT:PCBM:3 wt% PTBDTDPPSiCN(5/5) and (d) P3HT:PCBM:3 wt% PTBDTDPPSiCN(7/3)

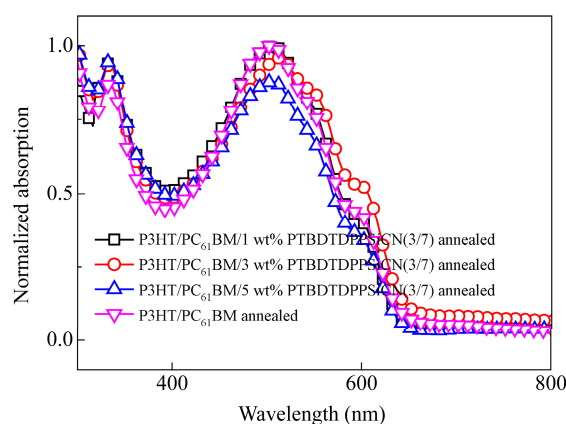


Fig. 6 UV-Vis absorption spectra of P3HT/PC₆₁BM/PTBDTDPPSiCN after annealing at 150 °C for 10 min

Photovoltaic Properties

The photovoltaic performance of P3HT:PC₆₁BM with three copolymers as additive in a device configuration of glass/ITO/ZnO/P3HT:PC₆₁BM:copolymer/MoO₃/Ag is measured to check the function of these novel copolymers. The choice of solution has a great influence on the photovoltaic performance of active layer^[28], so chlorobenzene was selected as the solution of the active layer because of the good solubility of the blends. Figure 7(a) shows the J - V curves for the best devices made from 10 mg/mL solutions of P3HT and PC₆₁BM with different ratios of additives in chlorobenzene (1 wt%, 3 wt% and 5 wt%). Figure 7(b) shows the schematic representation of device configuration. The device area was defined to be 0.04 mm² with a mask and the detailed fabrication procedures are described in the experimental section. The device performances are summarized in Table 4. The devices prepared from pristine P3HT: PC₆₁BM exhibits a PCEs of 2.8%, with a short-circuit current (J_{sc}) of 6.66 mA/cm, an open-circuit voltage (V_{oc}) of 0.628 eV, and a fill factor (FF) of 66.5%. After addition of these polymers into the active layer, there was no evident change of V_{oc} , while the PCEs of most devices have been obviously improved. The enhanced PCE is mainly related to the increased J_{sc} and FF. The enhanced device J_{sc} and FF should be attributed to the improved morphology of the active layer and the efficient charge transport properties due to these DPP-based copolymers, as mentioned above. Meanwhile, the bordered absorption from the additives also accounts for the J_{sc} enhancement. From the data we also can see that the devices with PTBDTDPPSiCN(3/7) and PTBDTDPPSiCN(5/5) show a relatively better performance than the one with PTBDTDPPSiCN(7/3), due to their more favorable nanostructure of the active layer, as evidenced by AFM observation. Figure 7(a) shows the J - V characteristics of photovoltaic cells based on P3HT:PC₆₁BM:polymer (with different mass ratios of polymer) blend films under AM 1.5 G illumination from a calibrated solar simulator with 100 mW/cm² (after thermal annealing at 150 °C for 10 min). Figure 7(b) is the schematic representation of device configuration. The amount of polymeric additives also impacts greatly on the device performance. Seen from the Fig. 7, Fig. S7 and Table 4, the devices with 3 wt% PBDTTPPSiCN(3/7) and PTBDTDPPSiCN(5/5) achieve the best PCE of 3.1% and 3.2%, respectively.

Further increasing the loadings of the additives sharply reduces the device efficiency. However, for the devices with PTBDTDPPSiCN(7/3), the optimal ratio of the additive is found to be 5 wt%, showing the best PCE of 3.1%. The strong additive loading dependency of the PCE can be well explained from the morphology change caused by the different loadings of the polymeric additives. In Fig. 8 and Fig. S8, among the AFM images of the copolymer modified P3HT:PC₆₁BM, the blends with 3 wt% PTBDTDPPSiCN(3/7) and PTBDTDPPSiCN(5/5) present the smoothest and most homogenous morphology of the blends. However, for the device with PTBDTDPPSiCN(7/3), the optimal morphology with a smallest roughness of 1.73 nm is developed by the 5 wt% PTBDTDPPSiCN(7/3), consequently achieving the best performance. Furthermore, the highest content of trimethoxysilyl groups can be transformed to organic Si—O—Si networks *via* thermal treatment, which is beneficial to stabilize the morphology of the active layer.

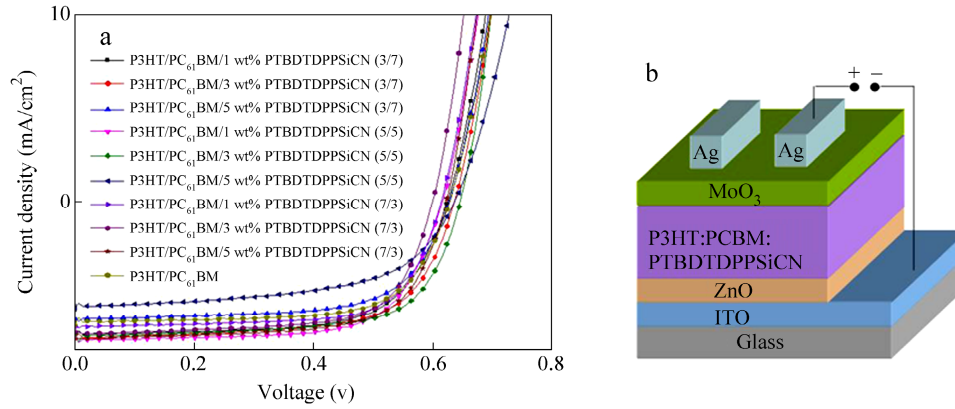
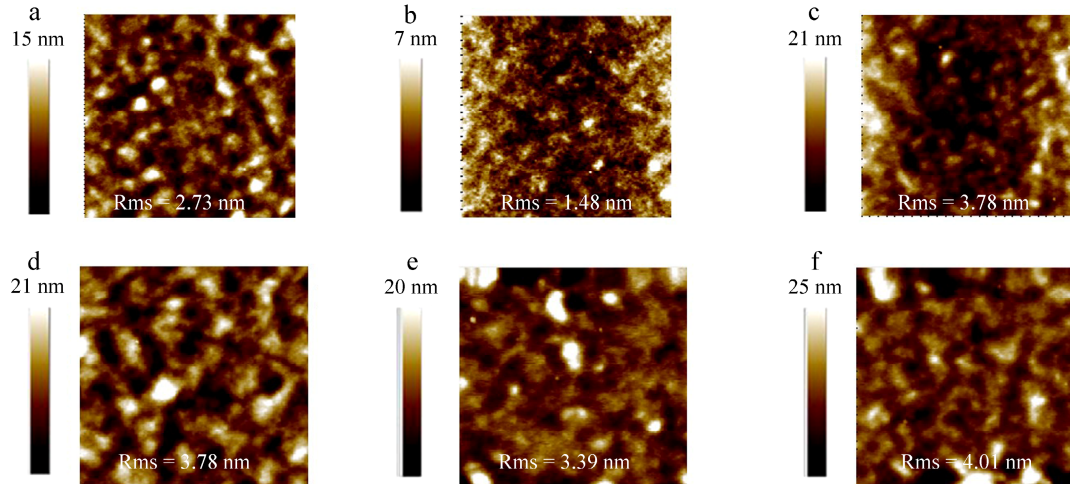


Fig. 7 (a) J - V characteristics of photovoltaic cells based on P3HT:PC₆₁BM:polymer (with different mass ratios of polymer) blend films under AM 1.5 G illumination from a calibrated solar simulator with 100 mW/cm²; (b) The schematic representation of device configuration

Table 4. The photovoltaic parameters for P3HT:PC₆₁BM:polymer BHJ devices

Device	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE _{max} (%)
P3HT: PC ₆₁ BM	6.66	0.628	66.5	2.8
with 1 wt% PTBDTDPPSiCN(3/7)	7.30	0.624	65.0	3.0
with 3 wt% PTBDTDPPSiCN(3/7)	7.36	0.636	65.6	3.1
with 5 wt% PTBDTDPPSiCN(3/7)	6.26	0.627	66.4	2.6
with 1 wt% PTBDTDPPSiCN(5/5)	7.19	0.616	70.5	3.1
with 3 wt% PTBDTDPPSiCN(5/5)	7.36	0.648	66.9	3.2
with 5 wt% PTBDTDPPSiCN(5/5)	5.68	0.636	57.1	2.1
with 1 wt% PTBDTDPPSiCN(7/3)	6.76	0.613	69.1	2.9
with 3 wt% PTBDTDPPSiCN(7/3)	7.01	0.599	69.0	2.9
with 5 wt% PTBDTDPPSiCN(7/3)	7.45	0.622	66.5	3.1

V_{oc} is the open-circuit voltage. J_{sc} is the short-circuit current. The fill factor (FF) is a graphic measure of the J - V curve.



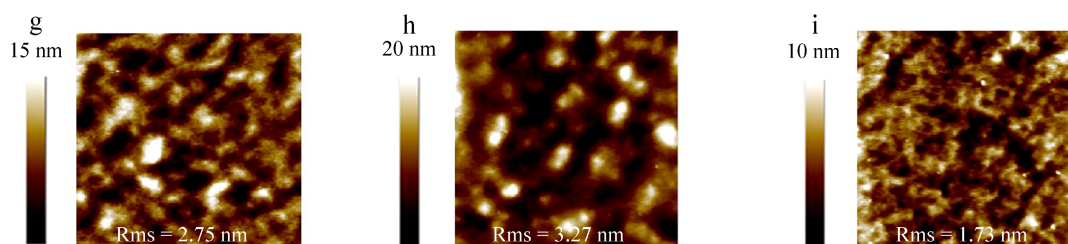


Fig. 8 Tapping mode AFM height images of the films based on P3HT: PC₆₁BM:polymer after annealing at 150 °C for 10 min (3 μm × 3 μm): (a) P3HT:PC₆₁BM: 1 wt% PTBDTDPPSiCN(3/7), (b) P3HT:PC₆₁BM: 3 wt% PTBDTDPPSiCN(3/7), (c) P3HT:PC₆₁BM:5 wt% PTBDTDPPSiCN(3/7), (d) P3HT:PC₆₁BM: 1 wt% PTBDTDPPSiCN(5/5), (e) P3HT:PCBM:3 wt% PTBDTDPPSiCN(5/5), (f) P3HT:PC₆₁BM:5 wt% PTBDTDPPSiCN(5/5), (g) P3HT:PC₆₁BM:1 wt% PTBDTDPPSiCN(7/3), (h) P3HT:PCBM:3 wt% PTBDTDPPSiCN(7/3) and (i) P3HT:PC₆₁BM:5 wt% PTBDTDPPSiCN(7/3)

CONCLUSIONS

In conclusion, a series of novel low band gap conjugated random copolymers are designed and synthesized, featuring random alternating TBDT units in conjugation with electron-deficient DPPCN and DPPSi moieties. These copolymers possess systematically tuned optical and electrical characteristics through the functionalization of cyano groups and siloxane groups on the side-chains. These copolymers exhibit low-lying HOMO energy levels and broad absorption bands which extend from the visible to the NIR-desirable properties. Incorporation of these novel copolymers as additives into the P3HT:PC₆₁BM blend is found to broaden the light absorption, improve the compatibility of the P3HT and PC₆₁BM and optimize the morphology of the active layer, subsequently leading to the improved device performance. These results indicate that the novel random copolymers are promising candidates as additives to optimize the morphology of the active layer for high performance organic photovoltaic devices.

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